The difference between theoretical and experimental values of ku is less than 10%, except again for runs 4 and 5, where the error is 15%. The agreement between the calculated and experimental values of fu and ku may at first appear poor, but when the error in estimating the quantities C_1, C_2, K_1, K_2, u and α is considered it is evident that the figures probably lie within the limits that would be expected.

Notation

A	Cross-sectional area of column (cm.^{2})
C_1	Concentration of reactant in liquid (mole/cm.^{3})
C_2	Concentration of reactant on resin (mole/cm.^{3})
F	Volume flow rate (ml./min.)
f	$= \alpha C_1/\{\alpha C_1 + (1 - \alpha)C_2\}$
$H(y)$	Heaviside unit step-function
K_1	Heat capacity of liquid (cal./cm.^{3} ° C)
K_2	Heat capacity of resin (cal./cm.^{3} ° C)
k	$= \alpha K_1/\{\alpha K_1 + (1 - \alpha)K_2\}$
Q	Heat of reaction (cal./mole)
T	Temperature (experimental) (° C)
t	Time (min.)
u	Linear flow velocity (cm./min.)
x	Distance along the tube (cm.)
α	Fraction void
δ	Dirac delta-function
ϕ	Rate of reaction function, i.e. rate of heat emission per unit volume of tube (cal./cm.^{3})
θ	Temperature rise (theoretical) (° C)

A consistent set of units are given in parentheses. Since concentrations appear as ratios in the final formulae, numerical values are in moles/litre.

Acknowledgment

The authors wish to thank the Directors of The Distillers Co. Ltd. for permission to publish this paper.

The Distillers Co. Ltd.
Research and Development Dept.
Great Burgh
Epsom, Surrey

Received 23 December, 1952

References

[1] Brinkley, S. R., *J. appl. Phys.*, 1947, **18**, 582
[2] Bjerrum, J. & Poulsen, K. G., *Nature, Lond.*, 1952, **169**, 463
[3] Anzelius, A., *Z. angew. Math. Mech.*, 1926, **6**, 291
[4] Schumann, T. E. W., *J. Franklin Inst.*, 1929, **208**, 305
[5] Furnas, C. C., *Bull. U.S. Bur. Min.*, No. 361, 1932
[6] Beaton, R. H. & Furnas, C. C., *Industr. Engng Chem.*, 1941, **33**, 1500

THERMODYNAMICS OF FORMALDEHYDE MANUFACTURE FROM METHANOL

By ELWYN JONES and G. G. FOWLIE

The production of formaldehyde from methanol, either by thermal decomposition, by catalytic oxidation or by a combination of the two, is treated as an exercise in chemical thermodynamics. Simple dehydrogenation of methanol does not appear attractive because it requires temperatures which tend to produce decomposition of the formaldehyde as it is formed. Oxidation of methanol to formaldehyde and steam requires the agency of a catalyst which is active in the region of 300°, the ideal working mixture for an insulated catalyst containing roughly 5½ to 8% of methanol in air. The composite

process, in which dehydrogenation and oxidation occur simultaneously, offers certain advantages, and may be expected to give maximum efficiency in the range 500–700°, corresponding to methanol/air mixtures containing 45 to 37% of methanol. Addition of steam to the reacting mixture lowers the catalyst temperature and modifies the product composition accordingly. Rapid cooling of the products to about 300° is essential to avoid regeneration of methanol and decomposition of formaldehyde. An interesting feature is that the straight oxidation-process operates with mixtures of methanol and air at or just below the lower inflammability limit, whereas the composite process requires mixtures at or above the upper inflammability limit.

Introduction

There are two stages of practical importance in the pyrolytic decomposition of methanol:

$$CH_3\cdot OH(g) \rightarrow H\cdot CHO(g) + H_2 \quad \Delta H \text{ (at } 298^\circ \text{ K)} = 21 \text{ kcal.}$$
$$H\cdot CHO(g) \rightarrow CO + H_2 \quad \Delta H \text{ (at } 298^\circ \text{ K)} = 2 \text{ kcal.}$$

and three stages of importance in its pyrolytic oxidation:

$$\tfrac{1}{2}O_2 + CH_3\cdot OH(g) \rightarrow H\cdot CHO(g) + H_2O(g) \quad \Delta H \text{ (at } 298^\circ \text{ K)} = -37 \text{ kcal.}$$
$$\tfrac{1}{2}O_2 + H\cdot CHO(g) \rightarrow CO + H_2O(g) \quad \Delta H \text{ (at } 298^\circ \text{ K)} = -56 \text{ kcal.}$$
$$\tfrac{1}{2}O_2 + CO \rightarrow CO_2 \quad \Delta H \text{ (at } 298^\circ \text{ K)} = -68 \text{ kcal.}$$

It will be noted that the dehydrogenation reactions are endothermic and the oxidation reactions exothermic. Consequently, if we aim to manufacture formaldehyde by the dehydrogenation of methanol, we must be prepared to supply heat at the rate of 21 kcal. per mole of formaldehyde; if we choose the oxidation process, we must make provision for the removal of 37 kcal. of heat per mole of formaldehyde. It would obviously be convenient if the two reactions could be combined in such a way that there is no need to make any such arrangements.

If the reactions were to occur at ordinary temperatures, this purpose could be achieved quite simply by combining oxidation and dehydrogenation in the proportions which would give zero heat of reaction:

$$37CH_3\cdot OH(g) + 21[\tfrac{1}{2}O_2 + CH_3\cdot OH(g)] \rightarrow 58H\cdot CHO(g) + 37H_2 + 21H_2O(g)$$
$$\Delta H \text{ (at } 298^\circ \text{ K)} = 0$$

There would then be no heat generated or absorbed, the temperature would be independent of throughput, and the only factor limiting output would be reaction rate.

At ordinary temperatures, the rates of these reactions are insignificant and so steps must be taken to accelerate them. Since the rate of a chemical process is normally an exponential function of the temperature, the logical course is to operate at elevated temperatures. One result of this will be that, in order to compensate for the heat carried away by the hot-product gases, an additional quantity of hydrogen must be consumed.

The problem is further complicated by the fact that the first and second stages in the pyrolytic decomposition of methanol, and the first and second oxidation stages, occur in temperature ranges which overlap; the result is that, under ordinary conditions, the formaldehyde is destroyed almost as quickly as it is formed. To freeze the formaldehyde, a way must be found to induce the primary decomposition, or the primary oxidation, of methanol to take place at a lower temperature level. This calls for the agency of a catalyst[1] and a convenient one would appear to be silver.[2]

It does not seem possible yet to predict the rate of the catalysed reaction and so estimate the production of formaldehyde per unit surface of catalyst per unit time. However, this difficulty is avoided if we assume that the surface area of the catalyst is large enough to ensure that thermodynamic equilibrium is reached before the gases leave the reactor. In practice, this can be arranged by adjusting the depth of the catalyst bed to suit the throughput.

Subject to the reservation that the size and depth of the catalyst are adjustable parameters, the problem of producing formaldehyde from methanol seems capable of solution by thermodynamic methods. This possibility has been examined by Vickery,[3] but on somewhat different lines from those which it is proposed to follow here.

Preliminary considerations

The equilibrium constant of the gaseous reaction

$$aA + bB \rightleftharpoons xX + yY$$

is given by $K = P_X{}^x P_Y{}^y / P_A{}^a P_B{}^b$

where A, B, X and Y are the chemical species involved, a, b, x and y are the respective quantities, in moles, taking part in the reaction, and P is the partial pressure of the reactant concerned.

At constant pressure $\ln K = -\Delta G^\circ / RT$, where ΔG° is the standard Gibbs function change.

It is not necessary here to enquire into the methods of evaluating ΔG°, as we are concerned only with numerical magnitudes and these, along with other relevant thermodynamic data, will be quoted from the literature.[4-6] It may be assumed, therefore, that K is known for all the reactions and at all the temperatures likely to concern us.

If we define A and B as the original reactants and X and Y as the reaction products, it will be apparent that, when K is very large, the equilibrium mixture will contain very little of the original reactants and the reaction may be regarded as substantially complete and irreversible. We shall indicate this in the following manner:

$$aA + bB \rightarrow xX + yY$$

On the other hand, when the value of K is near unity, i.e. when $\log_{10} K$ is approximately 0, the composition of the gas is very sensitive to variations in K, so that the reactions most likely to influence the quality of the product are those for which the value of $\log_{10} K$ passes through zero in the temperature range concerned. Such reactions will be represented thus:

$$aA + bB \rightleftharpoons xX + yY$$

Dehydrogenation method

The first stage in the pyrolytic decomposition of methanol is

$$CH_3 \cdot OH \rightleftharpoons H \cdot CHO + H_2$$

and the equilibrium mixture, corresponding to one mole of methanol originally, may be represented,

$$xH \cdot CHO + xH_2 + (1 - x)CH_3 \cdot OH$$

At atmospheric pressure, the equilibrium constant K is thus given by $K = x^2/(1 - x^2)$, which reduces to $x^2 = K/(1 + K)$.

The values of $\log_{10} K$ at different temperatures are given in Table I, so that x can now be evaluated for any chosen temperature. In other words, the composition of the equilibrium mixture can be predicted provided the temperature in the converter is known, and the effect of varying this temperature on the yield of formaldehyde can be calculated.

Table I

Thermodynamic equilibrium constants ($\log_{10}K$) for pyrolysis and oxidation of methanol

Chemical reaction	Temperature, ° K						
	600	700	800	900	1000	1100	1200
(1) $CH_3 \cdot OH \rightleftharpoons H \cdot CHO + H_2$	−1·22	−0·14	+0·69	+1·33	1·86	2·28	2·64
(2) $H \cdot CHO \rightarrow CO + H_2$	5·16	5·34	5·48	5·62	5·70	5·78	5·83
(3) $CH_3 \cdot OH + \frac{1}{2}O_2 \rightarrow H \cdot CHO + H_2O$	17·41	15·44	13·98	12·83	11·92	11·16	10·54
(4) $H \cdot CHO + \frac{1}{2}O_2 \rightarrow CO + H_2O$	23·79	20·92	18·77	17·12	15·76	14·65	13·73
(5) $CO + \frac{1}{2}O_2 \rightarrow CO_2$	20·06	16·54	13·90	11·84	10·20	8·86	7·74

The results of this calculation for temperatures between 300° and 1000° K are reproduced graphically in Fig. 1.

It will be evident from these results that the tendency towards dehydrogenation increases rapidly with rising temperature, and, if pyrolysis of methanol starts in the range of temperatures chosen, the first, or dehydrogenation, stage will be virtually complete at or above 1000° K. It is known[7] that decomposition of methanol begins at 500° (773° K), so that the required condition is, in fact, met. Consequently, if there were only one stage in the pyrolysis of methanol, formaldehyde could be produced simply by heating methanol vapour at some temperature above 1000° K, and, to avoid regeneration of methanol, rapidly condensing the formaldehyde.

Conversely, as the temperature falls, the proportion of methanol in the equilibrium mixture increases, so that the conditions in the lower range of temperatures favour the reverse reaction, namely the formation of methanol from formaldehyde and hydrogen. In fact, Newton & Dodge[8] have shown that, with the aid of a catalyst, formaldehyde is readily and almost completely hydrogenated in the temperature range 120–200° (390–470° K).

The second stage in the pyrolytic decomposition of methanol is $H \cdot CHO \rightarrow CO + H_2$.

This is shown as an irreversible process because, as will be seen from Table I, the equilibrium constant of this reaction has a value between 10^5 and 10^6. Given favourable conditions, therefore, this reaction will go virtually to completion. It is known that formaldehyde vapour starts to decompose at 300° (573° K), so that at 1000° K, the temperature considered necessary for reasonably complete dehydrogenation of methanol, the formaldehyde produced would be liable to be destroyed almost as quickly as it is formed.

It thus appears that, as a potential process for the manufacture of formaldehyde, straight dehydrogenation is not attractive, and the failure of all attempts to evolve a practical method on these lines confirms this conclusion.[1]

Oxidation method

In the straight oxidation method, the aim is, with the aid of a catalyst, to induce the primary stage in the oxidation of methanol to take place rapidly at temperatures below those at which the second stage occurs at an appreciable rate. This is possible because the primary stage becomes a heterogeneous reaction whereas the second stage remains homogeneous. According to our view, the second stage is the oxidation of the hydrogen liberated in the pyrolytic decomposition of formaldehyde, so that the critical temperature for the second oxidation stage is that at which formaldehyde decomposes. It has already been stated that pure formaldehyde vapour begins to decompose at 300° (573° K) and, for the present, we shall take this figure.

Atmospheric oxygen is the obvious choice for use in a commercial oxidation process and, for simplicity, air will be taken to consist of one part of oxygen to four parts of nitrogen. The basic reaction may, therefore, be represented:

$$CH_3 \cdot OH + \tfrac{1}{2}(O_2 + 4N_2) \rightarrow H \cdot CHO + H_2O + 2N_2$$

The use of the reactants in these proportions is impracticable because the mixture is explosive. The safety aspect has been discussed elsewhere[9] and need not be considered. The problem here is to bring the temperature of the products of this reaction down to the level at which decomposition of formaldehyde is negligible, i.e. to 573° K. To do this, heat must be removed during the reaction so that the temperature does not rise above this figure. At this temperature, the hot products would take away approximately 9 kcal. of heat per mole of formaldehyde, leaving 28 kcal. per mole to be disposed of in some other way.

Theoretically, the conventional solution is to connect the catalyst bed to a heat-sink, ideally at 573° K, but a little consideration will show that this is not practicable. For instance, if the throughput is doubled, twice as much heat must be removed, and so the rate of heat transfer must adjust itself automatically to the flow of gas, otherwise the temperature gets out of control. Moreover, unpredictable factors like weather conditions, which affect the flow of heat to earth, are liable to have a disturbing influence on plant operation. These considerations indicate that the only practical solution is to use the reaction-products as the heat-sink and insulate the catalyst bed; only in this way will the plant tolerate fluctuations in throughput without change in temperature. If the catalyst cannot be insulated, the same effect can be obtained by increasing the throughput until the heat leaking through the catalyst is small in comparison with the total heat generated. Thus, an uninsulated plant should give more consistent results at high production-rates, provided the catalyst bed is deep enough.

It follows therefore that the preferred method in practice is to dilute the reactants until the reaction temperature drops to about the critical value, which we have taken as 573° K. The cheapest and most convenient diluent is air, and if to each mole of methanol we add a volume of air equivalent to $\frac{1}{2}x(O_2 + 4N_2)$, the result of the reaction would be

$$CH_3 \cdot OH + \frac{x}{2}(O_2 + 4N_2) \rightarrow H \cdot CHO + H_2O + \frac{(x-1)}{2}O_2 + 2xN_2$$

in which the products are now assumed to be at 573° K.

The heats of reaction at different temperatures for this and other reactions of present interest are given in Table II, and the heat contents of the relevant gases and vapours are shown in Table III.

The change in heat content of the reactants between 298° K (in accordance with modern practice, this is taken as the normal temperature) and 573° K is given by

$$3 \cdot 68 + \frac{x}{2}(2 \cdot 007 + 4 \times 1 \cdot 935) = 3 \cdot 68 + 4 \cdot 873x$$

This, of course, is the heat of the reaction at 573° K, which is given as 36·7 kcal. On equating these two quantities we get $x = 6 \cdot 8$. If we are correct in our assumption that the critical temperature is 573° K, the ideal mixture to use in a straight oxidation process for the manufacture of formaldehyde from methanol is $CH_3 \cdot OH + 3 \cdot 4(O_2 + 4N_2)$, or 5·6% methanol in air.

The lowest temperature at which 100% formaldehyde vapour decomposes is 573° K, but the reaction is very slow at this temperature and would be slower still in the presence of inert diluents. At present, we are concerned with a diluent which contains an active ingredient, namely oxygen. The minimum ignition temperature of formaldehyde in air is also about 573° K, as might be expected. Again, this figure corresponds to the most favourably proportioned mixture of formaldehyde and air. In lean mixtures, the ignition temperature is higher and it may be expected that the catalyst temperature can be allowed to rise substantially above 573° K.

Table II

Heat of reaction (kcal.) at constant pressure for reactions occurring in the manufacture of formaldehyde

Chemical reaction	Temperature, ° K							
	500	600	700	800	900	1000	1100	1200
(1) $CH_3 \cdot OH \rightleftharpoons H \cdot CHO + H_2$	−21·5	−21·8	−22·0	−22·1	−22·2	−22·3	−22·4	−22·4
(2) $H \cdot CHO \rightarrow CO + H_2$	−2·2	−2·6	−2·8	−3·0	−3·1	−3·1	−3·1	−3·0
(3) $CH_3 \cdot OH + \frac{1}{2}O_2 \rightarrow H \cdot CHO + H_2O$	36·8	36·7	36·7	36·8	36·9	36·9	37·0	37·1
(4) $H \cdot CHO + \frac{1}{2}O_2 \rightarrow CO + H_2O$	56·1	55·9	55·9	55·9	56·0	56·1	56·3	56·5
(5) $CO + \frac{1}{2}O_2 \rightarrow CO_2$	67·80	67·79	67·76	67·70	67·64	67·55	67·45	67·35

Table III

Heat contents (kcal./mole) of gases and vapours involved in the manufacture of formaldehyde

Gas or vapour	Heat content (kcal./mole) at temperature, ° K									
	300	400	500	600	700	800	900	1000	1100	1200
Oxygen	2·083	2·792	3·524	4·279	5·058	5·856	6·670	7·497	8·335	9·184
Hydrogen	2·036	2·731	3·430	4·129	4·831	5·537	6·248	6·966	7·692	8·428
Nitrogen	2·085	2·782	3·485	4·198	4·925	5·669	6·428	7·203	7·992	8·793
Steam	2·382	3·194	4·025	4·882	5·771	6·690	7·635	8·608	9·606	10·630
Carbon monoxide	2·086	2·784	3·490	4·210	4·946	5·700	6·471	7·257	8·056	8·868
Carbon dioxide	2·254	3·195	4·223	5·323	6·481	7·690	8·939	10·222	11·535	12·874
Methanol	2·69	3·85	5·21	6·75	8·44	10·30	12·29	14·38	16·57	18·84
Formaldehyde	2·410	3·299	4·289	5·386	6·587	7·876	9·258	10·707	12·22	13·79

If the temperature of the catalyst is taken as 400° (673° K), then, calculating as before, the value of x is found to be approximately 4·6 and the appropriate amount of methanol in the mixture is 8·0%. Thus, the temperature range 300–400° corresponds to working mixtures in the range 5½–8% of methanol.

The straight oxidation method is the subject of a number of patents,[10] and it is interesting to note that the working temperatures are given as 250–450° and the gas composition as 5–10% of methanol in air.

Composite method

As indicated in the Introduction, it would be convenient if dehydrogenation and oxidation could be combined in such a way that their heats of reaction exactly balance at the temperature of reaction. It will be noted that we are at liberty to balance these reactions at any temperature we please, which means that we can, in effect, decide the temperature at which the process attains equilibrium. Moreover, the equilibrium state is stable, because a rise in temperature increases the rate of discharge of heat to the sink and a drop in temperature produces the opposite effect. Thus, the plant is likely to stabilize itself at the selected temperature, and our problem is merely to ascertain the best working temperature and the particular combination of the reactants that will produce it.

Table I shows that the equilibrium constant of the oxidation reaction

$$CH_3 \cdot OH + \tfrac{1}{2}(O_2 + 4N_2) \rightarrow H \cdot CHO + H_2O + 2N_2$$

has a numerical value of 10^{11} to 10^{17} in the range of temperature concerned, so that the oxidation part of the composite process will be complete and irreversible at all relevant temperatures. On the other hand, the equilibrium constant of the dehydrogenation reaction ranges from 10^{-1} to 10^{2}; therefore, if an excess of methanol is present in the reactants, the reaction products will contain methanol, formaldehyde, steam, hydrogen and nitrogen, all in thermodynamic equilibrium at the temperature of the reaction. If the ratio of formaldehyde to methanol in the products is $(1 + x)$ to y, the combined process may be represented:

$$\begin{aligned} CH_3 \cdot OH + \tfrac{1}{2}(O_2 + 4N_2) \\ + (x + y)CH_3 \cdot OH \end{aligned} \quad \rightarrow \quad \begin{aligned} H \cdot CHO + H_2O + 2N_2 \\ + xH \cdot CHO + xH_2 + yCH_3 \cdot OH \end{aligned}$$

which reduces to

$$(1 + x + y)CH_3 \cdot OH + \tfrac{1}{2}(O_2 + 4N_2) \rightarrow (1 + x)H \cdot CHO + yCH_3 \cdot OH + xH_2 + H_2O + 2N_2$$

The equilibrium constant of the dehydrogenation reaction at this temperature is given by

$$K = x(1 + x)/y(4 + 2x + y)$$

Since K is known at all relevant temperatures (Table I), this expression provides one relationship between the two unknowns, x and y. Another relationship between these two quantities is obtained, as before, from the heat-content figures of Table III, by equating the heat required to raise the reactants to the reacting temperature to the heat of reaction at that temperature (Table II). These two relationships enable us to evaluate x and y at any temperature and so plot the yield of formaldehyde against temperature and gas composition.

Before doing this, it is necessary to decide how we propose to produce gas mixtures containing a high proportion of methanol, remembering that the vapour pressure of methanol at ordinary temperatures is only about 120 mm., corresponding to a methanol concentration in the gas of roughly 16%. Evidently, the gas mixture must be preheated and, of course, any heat introduced in this way must be taken into account. Because we intend later to consider the introduction of steam and we shall then wish to avoid premature condensation, we shall assume that the gases will be preheated to a temperature of 110° (383° K).

Taking the temperature of the reaction as 1000° K we have

$$K = x(1 + x)/y(4 + 2x + y) = 10^{1\cdot86} \text{ (from Table I)} = 72\cdot4$$

Change in heat content of the reactants between 383° and 1000° K

= Heat of reaction of the oxidation reaction at 1000° K

+ Heat of reaction of the dehydrogenation reaction at 1000° K

$$= 36\cdot9 - 22\cdot3x$$

From the heat-content figures in Table III, this is equal to

$$(1 + x + y)10\cdot73 + \tfrac{1}{2} \times 4\cdot825 + 2 \times 4\cdot539$$

which reduces to

$$y = 1\cdot369 - 3\cdot078x$$

Substituting for y in the equilibrium constant equation, we finally get $x = 0\cdot443$ and $y = 0\cdot004$. Thus, at $T = 1000°$ K, the ideal process would be

$$1\cdot447CH_3\cdot OH + \tfrac{1}{2}(O_2 + 4N_2) \rightarrow 1\cdot443H\cdot CHO + 0\cdot004CH_3\cdot OH + 0\cdot443H_2 + H_2O + 2N_2$$

This calculation can be repeated for other assumed values of T and the results for temperatures of 600° to 1200° K are reproduced in Table IV. This Table shows how the temperature of the catalyst and the composition of the products vary with the proportion of methanol to air in the in-going mixture.

Table IV

Effect of reaction temperature on product composition

Temp., °K	Values of x	Values of y	In-going gas, moles $CH_3\cdot OH$	$\frac{1}{2}(O_2+4N_2)$	H_2O	$CH_3\cdot OH$, %	Gaseous products, moles H·CHO	$CH_3\cdot OH$	H_2	H_2O	N_2	H·CHO, %
600	0·83	2·92	4·75	1·00	—	65·5	1·83	2·92	0·83	1·00	2·00	21·3
700	0·92	0·35	2·27	1·00	—	47·6	1·92	0·35	0·92	1·00	2·00	31·0
800	0·77	0·051	1·82	1·00	—	42·2	1·77	0·051	0·77	1·00	2·00	31·7
900	0·61	0·004	1·61	1·00	—	39·2	1·61	0·004	0·61	1·00	2·00	30·8
1000	0·44	0·004	1·45	1·00	—	36·7	1·44	0·004	0·44	1·00	2·00	29·5
1100	0·30	0·003	1·30	1·00	—	34·2	1·30	0·003	0·30	1·00	2·00	28·2
1200	0·17	0·000	1·17	1·00	—	31·9	1·17	0·000	0·17	1·00	2·00	27·0
600	0·78	2·73	4·51	1·00	1·00	56·3	1·78	2·73	0·78	2·00	2·00	19·2
700	0·83	0·285	2·11	1·00	1·00	37·6	1·83	0·285	0·83	2·00	2·00	26·3
800	0·65	0·020	1·67	1·00	1·00	32·3	1·65	0·020	0·65	2·00	2·00	26·1
900	0·46	0·008	1·46	1·00	1·00	29·5	1·46	0·008	0·46	2·00	2·00	24·6
1000	0·22	0·003	1·22	1·00	1·00	25·9	1·22	0·003	0·22	2·00	2·00	22·4

The results in Table IV bring out certain points worth noting. First, the reaction temperature rises with decreasing proportion of methanol in the mixture and, although this is only to be expected, it is interesting to observe that the critical concentration at 1000° K is 36·7%. The upper explosion limit of methanol in air is 36·5%,[11] so that, above 1000° K, the working mixtures are explosive; i.e., this is the region where homogeneous exothermic reactions come into prominence. At the

limit of inflammability, the rate of the explosive reaction, expressed as a linear velocity, is only about 20 cm./sec.,[12] so that the homogeneous reaction can be outstripped by the heterogeneous reaction if the latter can cope with a gas flow in excess of this figure. It appears, therefore, that the gas flow through the converter will determine the margin by which the temperature of 1000° K can be exceeded in practice. Subject to this correction, 1000° K may be taken as the limiting temperature above which oxidation reactions leading to more highly oxidized compounds begin to assume significant proportions; above this temperature, conditions may be expected to degenerate.

Another interesting, and at first sight paradoxical, feature is the eventual decrease in hydrogen formation with increasing temperature. Although the equilibrium constant of the dehydrogenation reaction increases rapidly with temperature, the amount of methanol converted into formaldehyde by dehydrogenation soon begins to decrease. This illustrates the danger of arguing from chemical-equilibrium data without taking the physical conditions into account. Endothermic reactions, unlike the exothermic kind, can proceed only at a rate, and to an extent, dictated by the heat supplied. In the present instance, the oxidation reaction supplies not only the heat required by the pyrolytic reaction but also that discharged into the sink; as the latter increases, the heat available for dehydrogenation diminishes, although the thermodynamic conditions become increasingly favourable.

If the efficiency of the process is judged by the concentration of formaldehyde in the reaction products, the optimum working temperature would appear to be about 750° K, corresponding to a 45%-methanol/55%-air mixture. On the other hand, if the efficiency is measured by the proportion of methanol converted into formaldehyde, the temperature should be about 1000° K. The best working range would thus appear to be 750–1000° K, corresponding to the range of methanol/air mixtures 45–37%. Since these figures apply to an insulated catalyst, it may be expected that leakage of heat from the catalyst may necessitate a slight correction, in the sense that a lower concentration of methanol may be needed to produce the required catalyst temperature.

As steam is a convenient vehicle for introducing heat into a gas stream, it would be interesting to examine the effect of the presence of steam on the formaldehyde process. Assuming we introduce one volume of steam for every 2·5 volumes of air, the in-going mixture would be $(1 + x + y)CH_3 \cdot OH + \frac{1}{2}(O_2 + 4N_2) + H_2O$, this mixture entering the reactor at a temperature of 383° K as before. Taking the reaction temperature this time as 700° K, we have

$$K = x(1 + x)/y(5 + 2x + y) = 10^{-0.14} \text{ (from Table I)} = 0{\cdot}7244$$

Following the same procedure as before, we have

$$(1 + x + y)4{\cdot}79 + \tfrac{1}{2} \times 2{\cdot}386 + 2{\cdot}261 + 2{\cdot}715 = 36{\cdot}7 - 22{\cdot}0x$$

which reduces to

$$y = 4{\cdot}905 - 5{\cdot}594x$$

Substituting for y in the equilibrium-constant equation, we finally get $x = 0{\cdot}83$ and $y = 0{\cdot}285$. Thus, at $T = 700°$ K, the ideal process would be

$$2{\cdot}11CH_3 \cdot OH + \tfrac{1}{2}(O_2 + 4N_2) + H_2O \rightarrow 1{\cdot}83H \cdot CHO + 0{\cdot}285CH_3 \cdot OH + 0{\cdot}83H_2 + 2H_2O + 2N_2$$

Corresponding figures for temperatures between 600 and 1000° K are given in the lower part of Table IV; they show that the most important effect of adding steam to the methanol/air mixture is to lower the temperature of the catalyst. As would be expected, the chemical equilibria are determined mainly by the catalyst temperature and, except as a means of controlling this temperature, the introduction of steam seems to offer no special advantage.

Freezing of products

It has been pointed out that, above 300°, formaldehyde tends to decompose irreversibly into carbon monoxide and hydrogen. In the absence of a specific catalyst, this reaction occurs homogeneously in the gas phase and its rate will depend on the rate at which heat can pass into, and spread through, a poor heat-conductor. Thus, although the thermodynamic conditions favour the decomposition of formaldehyde, the poor conductivities of both catalyst and gas tend to retard this reaction and so preserve the formaldehyde.

As the products cool, however, the equilibrium constant of the reversible reaction

$$CH_3 \cdot OH \rightleftharpoons H \cdot CHO + H_2$$

falls very rapidly and methanol is now regenerated. Moreover, the reverse reaction is strongly exothermic and, being also homogeneous, not only provides the heat necessary to decompose

formaldehyde but also conveniently generates the heat homogeneously throughout the gas. Thus, gradual cooling of the products of the ' composite ' formaldehyde process will result in some formaldehyde recombining with hydrogen and some decomposing simultaneously into carbon monoxide and hydrogen. Once carbon monoxide is formed in the presence of steam, the water-gas reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

may come into play, with the formation of carbon dioxide and the liberation of more heat, to cause still more decomposition of formaldehyde.

Again, if the catalyst is overheated and the products of the catalytic reaction are at an excessively high temperature to start with, decomposition of formaldehyde can take place initially at the expense of the heat content of the gases themselves—another heat factor which is homogeneously distributed. The resulting absorption of heat lowers the temperature and so automatically reverses the methanol-dehydrogenation reaction, thereby initiating the train of reactions described above.

These considerations lead to the conclusion that an essential part of the ' composite ' formaldehyde process must be rapid cooling of the products to a temperature of about 300°, otherwise homogeneous reactions will occur with loss of formaldehyde, partly by regeneration of methanol and partly by thermal decomposition. The incidence of these adventitious reactions is indicated by the presence of methanol and oxides of carbon in the products.

An interesting distinction between the ' composite ' process and the straight oxidation process is that the former operates most efficiently near the upper explosive limit and the latter in the region of the lower explosive limit of methanol vapour/air mixtures.

Research Department
Imperial Chemical Industries Ltd., Nobel Division
Stevenston
Ayrshire

Received 29 October, 1952

References

[1] Green, S. J., ' Industrial Catalysis ', 1928 (London: Ernest Benn Ltd.)

[2] Walker, J. F., ' Formaldehyde ', Amer. chem. Soc. Monograph No. 98, 1944

[3] Vickery, B. C., *Industr. Chem. Mfr*, 1947, **23**, 141

[4] Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S. & Jaffe, I., U.S. Bureau of Standards, Circ. No. 500, 1952; ' Selected Values of Chemical Thermodynamic Properties '

[5] Smith, J. M., *Chem. Engng Progr.*, 1948, **44**, 521

[6] Thompson, H. W., *Trans. Faraday Soc.*, 1941, **37**, 251

[7] Hurd, C. D., ' The Pyrolysis of Carbon Compounds ', 1929 (New York: Chem. Cat. Co.)

[8] Newton, R. H. & Dodge, B. F., *J. Amer. chem. Soc.*, 1933, **55**, 4747

[9] Jones, E., *Chem. Engng*, 1952, **59**, (6), 185

[10] Craver, A. E., U.S.P. 1,383,059; 1,851,754

[11] White, A. G., *J. chem. Soc.*, 1922, **121**, 1244

[12] Payman, W., *J. chem. Soc.*, 1919, **115**, 1436

PHYSICOCHEMICAL STUDIES ON DUSTS. VI.* ELECTRON-OPTICAL EXAMINATION OF FINELY GROUND SILICA

By J. G. GIBB, P. D. RITCHIE and J. W. SHARPE

Changes in surface structure brought about by removal of the high-solubility layer from crystalline-quartz and fused-silica (Vitreosil) dusts by 40% hydrofluoric acid, and from Lochaline-sand dust by a borate buffer (pH 7·5), are studied by electron-optical methods. The accompanying changes in electron-diffraction pattern show that the original surface-layer is amorphous (estimated mean thickness about 0·03–0·06 μ); for quartz and Lochaline-sand dusts there is some evidence of an intermediate layer of very minute crystallites between the amorphous layer and the crystalline core.

* Part V: *J. appl. Chem.*, 1953, **3**, 182; Part IV: *J. appl. Chem.*, 1952, **2**, 658; Part III: *J. appl. Chem.*, 1952, **2**, 413